Catalytic Reactions of Cyclooctane and Ethylcyclohexane on HY Zeolite

INTRODUCTION

Few systematic studies of the reactions of cycloparaffins on zeolites have been reported, considering their importance as a component of commercial crude feedstocks (1). Studies of small ring (C_3, C_4) cycloparaffins (2, 3) have shown that the primary reaction product is the corresponding olefin. It has not been established, however, that the corresponding olefin is produced as an initial product of the cracking of medium-sized (C_5, C_6) rings.

Studies of cycloparaffin cracking on silica–alumina catalysts (4) report that the degree of saturation of low-molecular-weight products is much greater than that observed in comparable n-paraffin cracking. Reactions of methylcyclohexane on HY zeolite at 450°C have shown that dehydrogenation, isomerization, and cracking are all primary processes (5).

Here we report product distributions in the "cracking" of ethylcyclohexane and cyclooctane on HY zeolite at 400°C and compare product distributions for these cycloparaffins.

EXPERIMENTAL

Ethylcyclohexane (99.47% purity) and cyclooctane (99.83% purity) were obtained from Aldrich and used without further purification. Impurities present in ethylcyclohexane were methylcyclohexane, 0.382%; dimethylcyclohexanes, 0.055%; 2-methylpentane, 0.029%; 3-methylpentane, 0.033%; and n-hexane, 0.034%. Impurities in cyclooctane were ethylcyclohexane, 0.141%, and dimethylcyclohexane, 0.028%. HY zeolite was pre-

pared from NaY (Linde Co., lot No. 45912, SK40) by repeated exchanges with 0.5 N ammonium nitrate solution followed by calcination at 500°C. The sample used was found to have 97.3% sodium exchanged, by atomic absorption. Although a precise measurement of the level of crystallinity could not be made from X-ray diffraction data, major structural collapse of the zeolite did not occur at temperatures below 1000°C. After heat treatment at 1100°C for 24 h the sample was amorphous. Catalysts with mesh size 50/70 were steamed for 24 h at 200°C before use.

All experiments were performed at 400°C using an integral, fixed bed, gas phase, plug flow reactor with an independently controlled three-zone heater. The experimental apparatus and procedures used were similar to those described in previous studies (6). Blank runs were carried out at 400°C to ensure that the glass used to dilute the catalyst was inert.

Liquid products were analyzed by a Varian gas chromatograph with a 60-m SE54 capillary column and flame ionization detector. Analysis of coke was carried out using previously described procedures (7).

DISCUSSION OF RESULTS

Isomerization

Optimum performance envelopes (6) were plotted for all products of reaction. Examples are presented in Figs. 1 and 2. The characteristics of these envelopes enable the product type (primary or secondary, stable or unstable) to be assigned in each case (6). These are presented in Tables 1 and 2 for isomerization and cracking
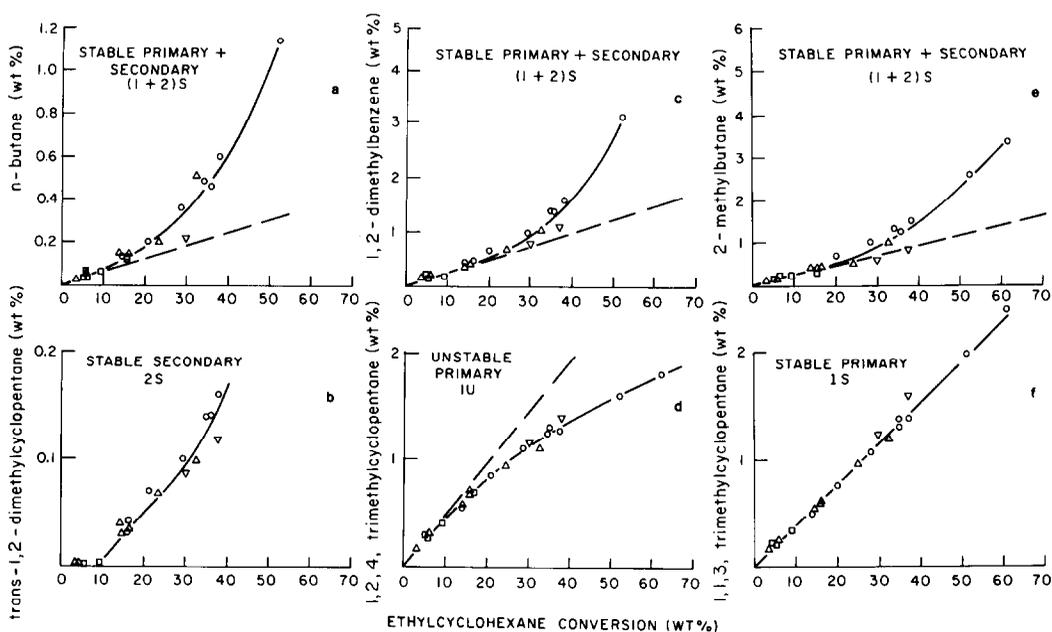
FIG. 1. Optimum performance envelopes for products of reaction of ethylcyclohexane on HY at 400°C. (a) *n*-Butane, (b) *trans*-1,2-dimethylcyclopentane, (c) 1,2-dimethylbenzene, (d) 1,2,4-trimethylcyclopentane, (e) 2-methylbutane, (f) 1,1,3-trimethylcyclopentane. Catalyst to reactant ratios: (□) 0.00150, (△) 0.00300, (▽) 0.0060, (○) 0.0121. Dashed lines indicate initial selectivities.

TABLE 1

Product Types and Initial Weight Selectivities for Isomerization of Cyclooctane and Ethylcyclohexane on HY

Product	Type[a]		Initial selectivity	
	Cyclooctane	Ethyl-cyclohexane	Cyclooctane	Ethylcyclohexane
Cyclopentane rings				
1,1,2-Trimethylcyclopentane	(1 + 2)S	1S	0.0100	0.0098
1,1,3-Trimethylcyclopentane	(1 + 2)S	1S	0.0298	0.0375
1,Methyl,*trans*-2-ethylcyclopentane	1S	1S	0.0298	0.0261
1-Methyl,*cis*-2-ethylcyclopentane	1U	1U	0.0228	0.0292
1-Methyl,*trans*-3-ethylcyclopentane	1U	1U	0.0713	0.0686
1-Methyl,*cis*-3-ethylcyclopentane	(1 + 2)S	1U	0.0489	0.0615
1,*trans*-2,*cis*-3-Trimethylcyclopentane	(1 + 2)S	1S	0.0290	0.0302
1,*cis*-2,*cis*-3-Trimethylcyclopentane	1U	1U	0.0079	0.0076
1,*cis*-2,*trans*-3-Trimethylcyclopentane	1U	1U	0.0372	0.0532
1,*cis*-2,*cis*-4-Trimethylcyclopentane				
1,*trans*-2,*cis*-4-Trimethylcyclopentane	(1 + 2)S	1U	0.0745	0.0939
1,*cis*-2,*trans*-4-Trimethylcyclopentane	2S	(1 + 2)S	—	0.0057
Isopropylcyclopentane	1U	1U	0.0133	—
n-Propylcyclopentane	1S	—	0.0309	—
			0.4054	0.4381
Cyclohexane rings				
1,1-Dimethylcyclohexane	1S	1U	0.0468	0.0636
1,*trans*-4-Dimethylcyclohexane	1S	1U	0.1319	0.1241
1,*cis*-3-Dimethylcyclohexane	(1 + 2)S	1S	0.0100	0.0073
1,*trans*-2-Dimethylcyclohexane	1S	1U	0.0436	0.0427
1,*trans*-3-Dimethylcyclohexane	1U	1U	0.1234	0.1528
1,*cis*-4-Dimethylcyclohexane				
1,*cis*-2-Dimethylcyclohexane	1U	1U	0.0298	0.0386
Ethylcyclohexane	1U	—	0.1148	—
			0.5003	0.4291
Total			0.9057	0.8672

[a] 1, primary; 2, secondary; S, stable; U, unstable.
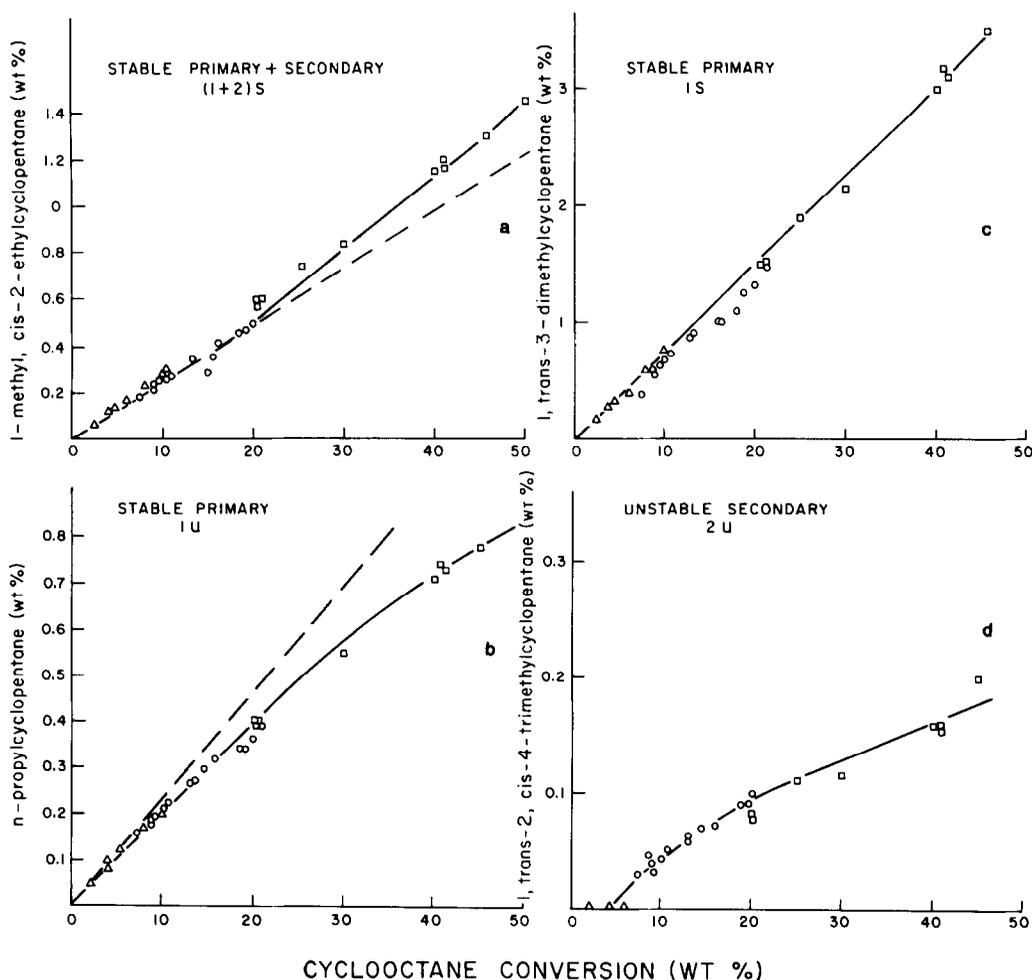
FIG. 2. Optimum performance envelopes for products of reaction of cyclooctane on HY at 400°C. (a) 1-*methyl*, *cis*-2-Ethylcyclopentane, (b) *n*-propylcyclopentane, (c) 1,*trans*-3-dimethylcyclopentane, (d) 1,*trans*-2,*cis*-4-trimethylcyclopentane. Catalyst to reactant ratios: (△) 0.00147, (○) 0.00294, (□) 0.00588. Dashed lines indicate initial selectivities.

processes, respectively. All the impurities also appeared as products of reaction on HY zeolite at 400°C, and their presence in the feed was taken into account when calculating initial selectivities.

(i) *Ring contraction of cyclooctane.* The dominant initial reaction of cyclooctane on HY zeolite at 400°C is ring contraction, accounting for over 90% of the initial selectivity. Individual initial selectivities for the product isomeric cyclopentanes and cyclohexanes are given in Table 1.

Ring contraction has been extensively studied for cycloparaffins in liquid media.

Solvolysis of medium ring (8–11 membered) cycloalkyl derivatives occurs at faster rates than that of the common ring (5–7 membered) or large ring (12+ membered) cycloalkyl derivatives (8). Studies of ring contraction in 7- to 12-membered cycloalkanes at 30°C using an $AlBr_3$ catalyst have shown that the rate depends on ring size, being highest for cyclooctanes (9). These results were interpreted as arising from the relief of ring strain (10–12). Calculated ring strain estimates show a minimum of strain for 6-membered rings, and maxima for small rings (3 and 4 membered) and

TABLE 2

Product Types and Initial Weight Selectivities for Cracking of Cyclooctane and Ethylcyclohexane on HY

Product	Type[a]		Initial selectivity	
	Cyclooctane	Ethylcyclohexane	Cyclooctane	Ethylcyclohexane
C_2				
Ethylene	—	(1 + 2)S		0.0022
Ethane	2S	—		—
C_3				
Propane	(1 + 2)S	(1 + 2)S	0.0030	0.00522
Propylene	1U	1U	0.0100	0.00937
C_4				
n-Butane	(1 + 2)S	(1 + 2)S	0.0071	0.00667
Isobutane	1S	(1 + 2)S	0.0200	0.0213
C_4 olefins	2U	2S		
C_5				
n-Pentane	2S	2S		
2-Methylbutane	(1 + 2)S	(1 + 2)S	0.0212	0.0255
C_6				
C_6 paraffins	2S	(2)S	—	
Methylcyclopentane	2S	(1 + 2)S	—	0.00713
Cyclohexane	2S	2S	—	—
C_7				
C_7 paraffins	2S	2S		
1,3-Dimethylcyclopentane	2S	2S		
1,2-Dimethylcyclopentane	2S	2S		
Ethylcyclopentane	2S	2S		
Methylcyclohexane	2S	(1 + 2)S		0.0055
C_8				
2,5-Dimethylhexane	2S	2S		
C_8 aromatics	(1 + 2)S	(1 + 2)S	0.0276	0.0318
C_9 aromatics	2S	(1 + 2)S		0.00638
Coke			0.0060	0.0050
			0.0949	0.1261

[a] 1, primary; 2, secondary; S, stable; U, unstable.

medium-sized rings (8 or 9 membered) (9, 11). The reported high selectivity for ring contraction of cyclooctane shows this to be the preferred mechanism for relief of ring strain. In contrast ring cleavage is observed for small ring cycloalkanes (2, 3). For example, reaction of cyclopropane on 13X zeolite gave propylene as the only primary product (2). We have found no trace of C_8 olefins in our studies of the reaction of cyclooctane on HY at 400°C or at 295°C.

Results presented in Table 1 show that at 400°C on HY zeolite cyclooctane gives almost equal yields of isomeric product dis-

tributions from cyclooctane and ethylcyclohexane suggests a common intermediate species in the mechanism of reaction for both cyclooctane and ethylcyclohexane.

NMR studies of acid solutions of these hydrocarbons and of methylcycloheptane (15) have shown that very similar active species are present in all these cases. Quenching of the reactions at low temperatures followed by isolation and characterization of the product revealed that 1-ethylcyclohexanol was produced in each case, indicating that the 1-ethylcyclohexyl cation is the common species formed from all these molecules in liquid acid media. This

species is probably also the common intermediate on solid acids, which explains why our observed product distributions are very similar to those formed in liquid acid media. It should be noted that no species having a seven-membered ring was identified in our products from either feedstock.

DISCUSSION OF THE MECHANISM

Isomerization Mechanism

Most of the primary isomerization product can be explained by assuming the initial formation of a secondary or tertiary carbocation, followed by a series of ring contractions and expansions requiring only five- and six-membered ring intermediates. This is the mechanism proposed by Pines and Shaw (16) for the hydroisomerization of isotopically labeled ethylcyclohexanes on a nickel–silica–alumina catalyst at 360°C.

However, the primary products 1,1-dimethylcyclohexane and isopropylcyclohexane require either the formation of a primary carbocation or the expansion to a metastable seven-membered ring structure.

The observed high content of 1,1,3-trimethylcyclopentane relative to 1,1,2-trimethylcyclopentane formed by isomerization of C_8 cycloparaffins has been attributed to cis-vicinal interaction of the methyl groups in the 1 and 2 positions of the 1,1,2 isomer (13). Our initial selectivities in Table 1 show that the 1,1,3 isomer is preferentially formed from both cyclooctane and ethylcyclohexane at 400°C, the selectivity ratios being 3.0 and 3.8 respectively in favor of this isomer. At 295°C the ratio of these initial selectivities was 4.5 from cyclooctane. Similar steric interactions will explain the predominance of 1, trans-2, cis-3-trimethylcyclopentane over the 1, cis-2, cis-3 isomer. Ratios of initial selectivities at 400°C for these isomers were found to be 3.7 and 4.0 from cyclooctane and ethylcyclohexane reactions, respectively.

Cracking Mechanism

The reaction products from cracking of ethylcyclohexane and cyclooctane are given in Table 2 which shows that total selectivities for cracking are similar. No methane or molecular hydrogen was observed as either primary or secondary products. The major initial products are either paraffins or aromatics. Ethylene and propylene were the only olefins observed as primary products. No olefins larger than C_4 were observed at any level of conversion. Methylcyclopentane and methylcyclohexane were the only observed primary cycloparaffin products of cracking, formed from ethylcyclohexane and cyclooctane, respectively. Cyclohexane, ethylcyclopentane, dimethylcyclopentane, and ethylcyclopentane were observed only as secondary products.

Initial selectivities for ring cleavage alone were 0.0613 and 0.0829 for cyclooctane and ethylcyclohexane, respectively (Table 2). This gives ratios for cleavage to isomerization of 0.068 and 0.096 for the two molecules, respectively, which is not in accord with the proposal that cyclic carbocations derived from five- or six-membered ring structures have an even chance of cracking or reverting to cyclic compounds (3). Indeed, at 295°C on HY, the selectivity ratio for cleavage to isomerization of cyclooctane was only 0.014, indicating that this ratio is temperature dependent, and cleavage becomes more significant at higher temperatures.

(i) *Monomolecular cracking.* Inspection of Table 2 shows that C_3, C_4, and C_5 fragments are the major initial products of cracking of cyclooctane and ethylcyclohexane. In addition the initial molar ratios for C_3/C_5 are close to unity (1.04 and 0.96, respectively) and it is reasonable to assume that the major initial modes of cracking can be represented by the monomolecular processes

$$C_8 \begin{array}{l} \nearrow C_3 + C_5 \\ \searrow C_4 + C_4 \end{array}$$
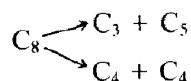
This mechanism accounts for all initial cracking products formed from cyclooctane. However, additional fragments (C_2, C_6, C_7, and C_9) are observed as primary cracking products from reaction of ethylcyclohexane.

The initial molar ratio for C_2/C_6 for reactions of ethylcyclohexane is close to unity (0.93) which suggests that formation of ethylene and methylcyclopentane occurs via a monomolecular cracking process

$$C_8 \rightarrow C_2 + C_6 \text{ (methylcyclopentane).}$$

A cracking mechanism leading to ethylene would require the initial formation of a primary carbocation on the side chain of ethylcyclohexane. This would explain the very low initial selectivity for the processes. Furthermore, this cracking mode is not observed in cyclooctane, as there is no side chain, and initiation involves the formation of a secondary carbocation on the ring itself.

(*ii*) *Disproportionation.* Table 2 shows that while C_7 (methylcyclohexane) is observed as a primary product from the reaction of ethylcyclohexane, there is no cor-

responding C_1 fragment. Methane was not detected at all in our work. However, the initial molar selectivity for C_9 fragments (trimethylbenzene) is very close to that of C_7. This suggests a disproportionation process (*17, 18*) accompanied by hydrogen transfer. A 1,2-dimethylcyclohexane carbocation can be formed from ethylcyclohexane via ring contraction and expansion. Once formed this can desorb directly or undergo desorption with hydrogen transfer to another species, leading to 1,2-dimethylcyclohexane or 1,2-dimethylbenzene as the observed primary products. Alternatively, a disproportionation and charge-transfer process with a gas phase ethylcyclohexane molecule can lead to trimethylbenzene and methylcyclohexane by a transfer of a methyl group from the side chain. The absence of a side chain on cyclooctane explains why this process is not observed as a primary process in the reaction of cyclooctane.

(*iii*) *Hydrogen transfer.* Hydrogen transfer was observed as an initial reaction of ethylcyclohexane and cyclooctane on HY at 400°C. This reaction was also previously

TABLE 3

Aromatic Products Identified in Concentrated Liquid Product from Cracking
C_8 Cycloparaffins on HY at 400°C

	Ethylcyclohexane	
C_8	C_9	C_{10}
Ethylbenzene	Trimethylbenzene	Dimethylethylbenzene
Dimethylbenzene	Ethylmethylbenzene	Tetramethylbenzene
	n-Propylbenzene	*t*-Butylbenzene
		Methylisopropylbenzene
C_{12}	C_{17}	
Ethyl-Np	Trimethylanthacene	
Dimethylnaphthalene		
	Cyclooctane	
C_8	C_9	C_{10}
Dimethylbenzene	Trimethylbenzene	Dimethylethylbenzene
	Ethylmethylbenzene	Tetramethylbenzene
		Methylisopropylbenzene
C_{11}	C_{12}	
Methylbutylbenzene		
Ethylisopropylbenzene	Dimethylnaphthalene	
Methylnaphthalene		

TABLE 4

Initial Hydrogen Transfer during Reaction of Cyclooctane, Ethylcyclohexane,
and n-Octane on HY at 400°C

	Moles H_2 transferred/moles feed converted	Initial selectivity		Hydrogen transferred/cracking selectivity
		Isomerization	Cracking	
Cyclooctane	0.0903	0.9057	0.0949	0.95
Ethylcyclohexane	0.107	0.8672	0.1261	0.85
n-Octane	0.100	0.0360	0.9773	0.10

reported in methylcyclohexane on HY at 450°C (5). During the hydrogenation paraffins are formed as C_3, C_4, and C_5 cracking products (Table 2), while the concurrent dehydrogenation forms aromatic species (Table 3). Initial C/H ratios for coke formation were found to be ~0.5 for both feedstocks, indicating mainly adsorbed reactant. The initial molar balance of the hydrogen present in acyclic paraffins to that lost by dehydrogenation to produce aromatics is close to unity for reaction of both cyclooctane (1.06) and ethylcyclohexane (0.93) as can be seen from the values presented in Table 4. Similarly to the case for reactions of n-alkanes on HY (19), we do not believe that any net transfer of hydrogen from the catalyst itself to form product species occurred. Furthermore catalyst activity was fully restored after regeneration in the presence of dry air, showing that all active sites bearing hydrogen were fully reconstituted after each experiment.

Table 4 shows that the total initial hydrogen transfer during reaction of ethylcyclohexane was greater than that for the reaction of cyclooctane. However, the ratios of hydrogen transfer to cracking are very similar, showing that hydrogen transfer is directly proportional to the rate of cracking which in turn is responsible for the production of olefin precursors which consume hydrogen while undergoing saturation. Table 4 also shows that the degree of hydrogen transfer associated with initial cracking processes is significantly higher for the C_8

cycloparaffins compared to the linear alkane (19).

CONCLUSIONS

Ring contraction and isomerization are respectively the dominant reactions of cyclooctane and ethylcyclohexane on HY zeolite at 400°C, forming five- and six-membered ring isomers with approximately equal probability. The similarity of initial product distributions for reactions of cyclooctane and ethylcyclohexane indicate that a common intermediate carbocation is formed. We believe this to be the tertiary ethylcyclohexyl carbenium ion. We believe this ion to be formed on Lewis sites only.

The major initial cracking products of both feeds are C_3, C_4, and C_5 paraffins. In both feeds hydrogen transfer during cracking is significantly higher than that which we observed for reactions of n-octane under the same conditions. This we attribute to the ease of hydrogen transfer from substituted cyclohexanes to saturate olefin precursors while the former undergo dehydrogenation to yield aromatics. No molecular hydrogen is produced by the initial reactions.

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